CLAIMS

[Claim(s)]
[Claim 1]A conductive resin composition containing a liquid crystal polymer and a conductive filler.
[Claim 2]The conductive resin composition according to claim 1, wherein said conductive fillers are one or more fillers chosen from a group which comprises black lead, Ketchen black, acetylene black, furnace carbon black, and thermal carbon black.
[Claim 3]The conductive resin composition according to claim 2, wherein said black lead is expanded graphite or granular graphite.
[Claim 4]The conductive resin composition according to any one of claims 1 to 3, wherein said liquid crystal polymer is liquid crystal polyester.
[Claim 5]The conductive resin composition according to any one of claims 1 to 4 in which loadings of said conductive filler are characterized by being 50 to 900 weight section to said liquid crystal polymer 100 weight section.
[Claim 6]The conductive resin composition according to claim 5 in which loadings of said conductive filler are characterized by being 100 to 600 weight section to said liquid crystal polymer 100 weight section.
[Claim 7]The conductive resin composition according to any one of claims 1 to 6 containing carbon fiber and/or glass fiber further.
[Claim 8]A separator for fuel cells comprising the conductive resin composition according to any one of claims 1 to 7.
[Claim 9]A sealing material comprising the conductive resin composition according to any one of claims 2 to 7.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]

[Field of the Invention]This invention relates to the separator for fuel cells and sealing material which consist of a conductive resin composition and said conductive resin composition.

[0002]
[Description of the Prior Art]In recent years, the demand about the fuel cell which carries out direct conversion of the chemical energy which fuel has to electric energy is increasing. Generally the fuel cell has composition which laminated many unit cells by which the electrode plate has been arranged on both sides of the matrix containing an electrolyte, and the separator has been arranged further at the outside. Usually, since fuel is supplied to one side of a separator and a gas oxidizer etc. are supplied to another field, a separator needs to excel in gas impermeableness so that both may not mix. Since a unit cell is laminated and used, for a separator to have high conductivity and to excel also in intensity is demanded.

[0003]The resin-molding article etc. which carried out mixed postforming of the glassy carbon and the end of carbon powder it is obtained by calcinating the mold goods conventionally produced by carrying out press forming of the black lead sheet as a separator for fuel cells, the resin impregnation material which impregnated the carbon sintered compact with resin, and thermosetting resin by an inert atmosphere, and the resin are used. For example, the separator which grows into JP,60-37670,A from thermosetting resin and carbon paper, such as phenol resin, to; JP,1-311570,A. The separator which blends expanded graphite and carbon black with thermosetting resin, such as phenol resin and furan resin, is indicated, respectively.

[0004]Fillers, such as black lead and carbon black, are used also as a raw material for sealing materials again. For example, if polymer, such as rubber, is filled up with carbon black, the degree of solvent swell of polymer can be improved, and the characteristics, such as intensity and abrasion resistance, can be attached. Black lead is a conformity reason to the outstanding slidability and flange surface, and a simple substance, or is used as sealing materials, such as packing and a vortex gasket, in the form of composite with polymer.

[0005]
[Problem(s) to be Solved by the Invention]However, in the separator for fuel cells, in resin impregnation material, cutting is needed and time and effort and cost start manufacture. If glassy carbon is used, the fabricating operation to a product configuration will become possible before calcination, but a problem produces the size contraction at the time of calcination, etc. in respect of dimensional stability. Although a resin-molding article is easy to fabricate, the fault inferior to conductivity is on account of the electric insulation of resin. If abundant restoration of the conductive filler is carried out that this point should be improved, shaping will become difficult or impossible. Also in a sealing material, abundant restoration of a filler brings about various advantages.

For example, abundant restoration of the carbon black can be carried out into rubber, and gas permeation-proof nature can be improved. In especially a black lead system sealing material, when obtaining high slidability and surface conformity, it is desirable to raise a black lead compounding rate as much as possible. Also in these sealing materials, problems, such as aggravation of a moldability and strength reduction, arise by abundant restoration of a filler.

[0006]This invention is made in view of such a situation, and is a thing.
** is easy for the purpose and it is providing the resin composition which is excellent in intensity, conductivity, and sealing nature, the cell for fuel which comprises it, and a sealing material.

[0007]
[Means for Solving the Problem]This invention persons are easy to fabricate by using a liquid crystal polymer, as a result of examining resin used for composite with a conductive filler that the above-mentioned purpose should be attained, For example, when it applied to a separator for fuel cells, or a sealing material, it found out that composite which is excellent with sufficient balance of required conductivity, gas-seal nature, and intensity was obtained. That is, this invention relates to a separator for fuel cells and a sealing material which consist of a conductive resin composition containing a liquid crystal polymer and a conductive filler and said conductive resin composition.

[0008]
[Embodiment of the Invention]Hereafter, this invention is explained in detail. In this invention, it is important requirements to use a liquid crystal polymer as a resinous principle. As the example which carries out a postscript also shows, even if it uses other polymer as a resinous principle, the composite which has physical properties which this invention makes the purpose, such as high conductivity, high intensity, and shaping ease, cannot be obtained. On the other hand, the constituent which is excellent with sufficient balance of physical properties, such as conductivity, gas-seal nature, and intensity, can be obtained by using a liquid crystal polymer as a resinous principle according to this invention. And in comparison with the conductive resin composition which uses thermosetting resin as a resinous principle, even if compared with the conductive resin composition which uses thermoplastics as a resinous principle, of course, it becomes easy manufacture and fabricating the conductive resin composition of this invention. The resinous principle by which the volume resistivity of the liquid crystal polymer itself is used for the conventional conductive resin composition. In spite of being high compared with (for example, the polyamide mentioned as the comparative example, polybutylene terephthalate, and polyester system thermoplasticity Hellas Maher), the conductivity which excelled the complex with the conventional resinous principle in the complex with a conductive filler comes to be shown. These are not expected at all.

[0009]This liquid crystal polymer (LCP) is publicly known in itself. LCP is a general term for the polymer which shows a liquid crystal state at the time of melting, and it cannot draw with one structural formula. Also in this invention, the word called LCP includes all the polymer that shows liquid crystallinity. Two or more LCP can also be used together. LCP is solidified carrying out orientation in that direction and maintaining this orientation at the time of cooling solidification, when the molecular assembly arranged at the time of melting was formed and external force, such as shearing and extension, was received. Therefore, compared with other polymer, high mobility, a low coefficient of linear expansion, good dimensional accuracy, high intensity, heat resistance, fire retardancy, chemical resistance, etc. are shown. in addition -- if there is crystallinity when it solidifies -- crystalline LCP -- it will be referred to as amorphous LCP if there is nothing.

[0010]Although it is easily available from a commercial scene in LCP, commercial LCP is usually classified into Type IIa whose heat deflection temperature is the not less than 300 ** type I and 240-300 **, Type IIb which is 200-240 **, and Type III below 200 ** based on the heat deflection temperature. Any LCP of a type can be used in this invention. For example, when LCP of Types I and IIa is needed for shaping at low temperature, it uses LCP of Type III or IIb for the heat-resistant use demanded. Commercial LCP is a copolymer which comprises two or more sorts of monomers, and there are some into which imide bonding, carbonate combination, the amide bond, the urethane bond besides what comprises only an ester bond (liquid crystal polyester), etc. were introduced in the bond form. Although all of these LCP can be used in this invention, it is preferred to use liquid crystal polyester especially.

[0011]Liquid crystal polyester is also publicly known and Xydar of Nippon Oil Chemicals, Various products, such as Vectra of Polyplastics, Inc., a nova curate of Mitsubishi Engineering plastics, a rod run of Unitika, Ltd., and SUMIKASU Per of Sumitomo Chemical Co., Ltd., are marketed. Liquid crystal polyester Usually, a - O-phi-C (=O)-ingredient (here, phi shows the Para phenylene group) and;-O-phi-O -, -Upright ingredient;-O-m-phi-O [, such as O-phi-phi-O-, -C(=O)-phi-C (=O) -, and -C(=O)-phi-phi-C (=O) -,] -, -C(=O)-m-phi-C (=O) -, -C(=O)-m-phi-m-phi-C (=O) -, -O-m-phi-C(=O)-, - O-phi-O-phi-O -, - O-phi-C (=O)-phi-O -, -O-phi-C(CH3) 2-phi-O -, - O-m-phi-C (CH3) 2-phi-O -, -O-m-phi-C(=O)-phi-C (=O) -, -O-Np-O-, -O-Np-C(=O)-, -C(=O)-Np-C(=O)- (here), etc. Bent m-phi shows a meta-phenylene group and Np indicates a naphthyl group to be, It has structure to which copolymerization of the flexible chains, such as a Crankshaft ingredient, an ingredient which gave substituents, such as an alkyl group and a phenyl group, to these or;-O-R-O-, and -C(=O)-phi-O-R-O-phi-C (=O) - (here, R shows an alkylene group), was carried out. High-heat-resistance liquid crystal polyester of Type I mainly comprises a - O-phi-C (=O)-ingredient and an upright ingredient, and Type IIa contains the Crankshaft ingredient which has a naphthyl group in many cases. For example, an aliphatic group is generally included, liquid crystal polyester of structure like [- O-phi-C (=O)-] n[-C(=O)-phi-C (=O)-O-R-O-] m is classified into Type IIbIII, and its molding temperature is low and it is excellent in pliability. Liquid crystal polyester of the

type of a gap to describe above in this invention can also be used. There is no restriction in particular in the molecular structure, heat resistance, heat deflection temperature, a molecular weight, melt viscosity, etc. However, for the use of which heat resistance is required, it is preferred to use Type IIb or III and liquid crystal polyester containing especially an aliphatic group for the use as which liquid crystal polyester of Type I or IIa is required of pliability and mobility. When mobility is especially required, the melt viscosity in the temperature of 300 ** in shear rate 10 3 / second preferably Below 10 3 poise. Below 10 3 poise uses liquid crystal polyester below 10 2 poise by shear rate 10 3 / second preferably especially in shear rate 10 2 / second. By this, also when abundant restoration of the conductive filler is carried out, a good moldability and intensity can be held.

[0012]A conductive filler can also use various publicly known things. For example, the powder of metal, such as silver, nickel, copper, aluminum, iron, and stainless steel, A flake, textiles;SnO_2, ZnO, In_2O_3, the metallic-oxide; conductive coat type conductive filler of TiO_2; although the powder of a carbon system, textiles, a flake, etc. are mentioned, it is not limited to these. It is also possible to use together two or more conductive fillers.

[0013]However, in this invention, it is preferred to use the powder of a carbon system or a flake, for example, carbon black, black lead, etc. as a conductive filler. By using these carbon system filler, also when the corrosion resistance of a conductive resin composition is improved and it is used as a fuel cell etc., a side reaction can be prevented. One or more fillers more preferably chosen from the group which comprises black lead, Ketchen black, acetylene black, furnace carbon black, and thermal carbon black are used. By this, the constituent obtained is more excellent in conductivity. Among these, Ketchen black and acetylene black are developed as a conductive filler, and are obtained by the pyrolysis of incomplete combustion, such as natural gas, and acetylene, respectively. Furnace carbon black is a filler obtained by the incomplete combustion of a hydrocarbon oil or natural gas, and is classified into SAF, ISAF, IISAF, HAF, FF, FEF, MAF, GPF, SRF, CF, etc. according to particle diameter. Thermal carbon black is carbon of the large particle diameter obtained by the pyrolysis of natural gas, and FT carbon, MT carbon, etc. are mentioned as an example.

[0014]Although it is independent about any of these carbon system filler in this invention or two or more sorts may be mixed and used, black lead is especially used for black lead or Ketchen black preferably. There is no restriction in particular in the kind of this black lead, and black lead of any gestalten, such as granular graphite, scaly graphite, expanded graphite, and colloidal graphite, can be used. Use of the intercalated graphite which intercalated fluoridation graphite or various metal atoms, the halogen atom, the halogenated compound, etc. is also possible. Expanded graphite is what carried out extended processing of between the layers of a graphite crystal structure here, and

conductivity and especially lubricity are good. Also in the above-mentioned black lead, expanded graphite and especially granular graphite are preferred.

[0015]The loadings of a conductive filler have 50 to 900 preferred weight section to liquid crystal polymer 100 weight section. If the loadings of a conductive filler are less than 50 weight sections, satisfactory conductivity will not be obtained, but if 900 weight sections are exceeded, a problem will be produced in respect of a moldability or intensity. As for especially the loadings of a conductive filler, when these points are taken into consideration, it is preferred especially to consider it as 200 to 500 weight section 100 to 600 weight section.

[0016]The conductive resin composition of this invention can also strengthen the mechanical strength of the mold goods (for example, the separator for fuel cells and a sealing material) by blending textiles further. For example, if carbon fiber and/or about 10-50 weight sections of glass fibers are especially blended one to 100 weight section to liquid crystal polymer 100 weight section, the intensity of the mold goods obtained, especially shock resistance are improvable. There is no restriction in particular in the kind of carbon fiber and glass fiber, and various publicly known textiles can be used. Otherwise, cotton, wool, silk, hemp, a nylon fiber, an aramid fiber, the vinylon (polyvinyl alcohol) textiles, Polyester fiber, a rayon fiber, an acetate fiber, phenolformaldehyde textiles, It is also possible to use textiles, such as polyphenylene sulfide fibers, acrylic fibers, polyvinyl chloride textiles, polyvinylidene chloride textiles, a polyurethane fiber, and tetrafluoroethylene textiles. However, in this invention, it is preferred to use carbon fiber especially PAN system carbon fiber, and a pitch based carbon fiber. Intensity can be improved by this, without spoiling most conductivity of mold goods. Although there is no restriction in particular also in the shape of textiles, length uses especially preferably the textiles within the limits which are about 0.1-20 mm about 0.01-100 mm. When less [if a fiber length exceeds 100 mm shaping will be difficult and will become difficult to make the surface smooth, and] than 0.01 mm, it becomes impossible to expect a reinforcing effect.

[0017]Otherwise in the conductive resin composition of this invention, other polymer as an arbitrary ingredient, For example, PET, PBT, thermoplastic elastomer polyester, low-molecular-weight polyester, A filler, for example, silica, besides;, such as polyamide, nitrile rubber, and acrylic rubber, Fillers, such as calcium carbonate, barium sulfate, and a viscosity mineral, paints, etc.; plasticizers, such as a dispersing agent, an antiaging agent, a coupling agent, a compatibilizer, fire retardant, a smooth surface agent, fatty acid, the ester, phthalic ester, plastic powder, processing aid, etc. can also be blended further.

[0018]The conductive resin composition of this invention can be manufactured by the method of various common use. Generally, heat melting of LCP is carried out, it kneads, and a conductive filler, textiles, etc. are added. Typically, LCP is fused with a kneader, a

Banbury mixer, an extrusion machine, a heating roller, etc., and a conductive filler, textiles, etc. are added under kneading there.

[0019]Like the above, the conductive resin composition of this invention constituted is easy to fabricate, and its conductivity is high, and it is excellent in intensity and gas impermeableness. So, it is the optimal as a material of the separator for fuel cells. Among the conductive resin compositions of this invention, the thing using a carbon system filler, especially black lead as a conductive filler is excellent in gas impermeableness etc., and also it has good slidability and surface conformity. So, it is useful also as a sealing material, especially packing.

[0020]A molding method in particular is not restricted but can fabricate injection molding, extrusion molding, transfer molding, blow molding, press forming, injection press shaping, extrusion injection molding, etc. in the field of thermoplastics to various kinds of shape with general-purpose various molding methods. Two or more these molding methods may be combined. For example, the Motoshige form of the sheet like object which could also make carry out melt adhesion of the mold goods obtained by injection molding or extrusion molding, and was obtained by extrusion molding or press forming may be carried out to the article of complicated uneven shape by press forming etc. If it is a person skilled in the art, according to a use and shape, it will be possible to select a desirable molding method and process condition. Since it has the strong point said that melt molding is possible, it is useful especially as materials, such as a thick material along which a complicated-shaped article and heat cannot pass easily. Recycling of a cast and reuse of the Bali portion etc. are also possible. Hereafter, although an example explains this invention in more detail, this invention is not limited to the following examples.

[0021]
[Example][Examples 1-6, the comparative examples 1-5]
- The constituent with expanded graphite was created using resin of preparation various kinds of a sample. The description of the used resin is shown below.
LCP-1 : Liquid crystal polyester of Type III, volume resistivity 1x10 17 omega-cm, Heat-deflection-temperature [of 120 **], and specific gravity 1.38LCP-2 : Liquid crystal polyester of Type III, Volume resistivity 6x10 16 omega-cm, the heat deflection temperature of 170 **, Specific gravity 1.41LCP-3 : Liquid crystal polyester of Type IIb, volume resistivity 1x10 17 omega-cm, Heat-deflection-temperature [of 210 **], and specific gravity 1.38PA-1 : The polyamide 6, volume resistivity 1x10 15 omega-cm, Specific gravity 1.14PA-2 : The polyamide 66, volume resistivity 1x10 14 omega-cm, Specific gravity 1.15PA-3 : The polyamide 12, volume resistivity 1x10 16 omega-cm, Specific gravity 1.06PBT : Polybutylene terephthalate, volume resistivity 1x10 16 omega-cm, Heat deflection temperature of 60 **, specific-gravity 1.31TPEE: Measure thermoplastic elastomer polyester, volume resistivity 1.8x10 12 omega-cm, specific gravity 1.15, in addition the above-mentioned volume resistivity according to ASTM

D257. Heat deflection temperature is the value measured in load 18.6 kgf/cm2 according to ASTM D648.

[0022]And expanded graphite of the specified quantity was added, kneading each of above-mentioned resin at 30 rpm with the temperature more than melting temperature among the mill provided with heating apparatus, as shown in Table 1. After all the kneading during 15 minutes, kneaded material was taken out, specified quantity restoration was carried out into the mold, it fabricated on a 100x100x2-mm sheet with heat pressing, and the sample was obtained. When manufacturing a sample, the quality of the flow nature within the difficulty of kneading and the mold at the time of a press was judged simultaneously. The piece of a sample blank test was taken out and bending strength and volume resistivity were measured according to ASTM D790 and JISK7194, respectively. The examination on gas transmittance was also done depending on the sample. Evaluation of gas transmittance was performed by measuring the transmission quantity of N2 gas which passes the sample of 2-mm thickness under the application of pressure of 1 kgf/cm2. A unit is a part for ml/. The difficulty at the time of manufacturing each sample (quality of the flow nature within the difficulty of kneading and the mold at the time of a press) and the physical properties of a sample are shown in Table 1.

[0023]

表 1：各サンプルの製造容易性・物性

		実施例1	実施例2	実施例3	比較例1	比較例2	比較例3	比較例4	比較例5	実施例4	実施例5	実施例6
配合	LCP−1	25.0	—	—	—	—	—	—	—	30.0	40.0	12.5
	LCP−2	—	25.0	—	—	—	—	—	—	—	—	—
	LCP−3	—	—	25.0	—	—	—	—	—	—	—	—
	PA−1	—	—	—	25.0	—	—	—	—	—	—	—
	PA−2	—	—	—	—	25.0	—	—	—	—	—	—
	PA−3	—	—	—	—	—	25.0	—	—	—	—	—
	PET	—	—	—	—	—	—	25.0	—	—	—	—
	TPEE	—	—	—	—	—	—	—	25.0	—	—	—
	膨張黒鉛	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	70.0	60.0	87.5
製造	混練難易	容易	容易	容易	容易	容易	容易	やや難	やや難	容易	容易	やや難
	プレス内流れ性	良好	良好	良好	良好	やや悪	悪	悪	やや悪	良好	良好	やや悪
物性	曲げ強さ(kgf/cm²)	232	287	341	187	153	151	134	197	268	371	149
	体積固有抵抗(mΩ cm)	10	8	19	70	80	100	120	47	35	55	2
	気体透過度(ml/分)	0.01	0.01	—	—	—	—	—	—	—	0.00	—

[0024]The sample which uses LCP as a resinous principle according to this invention is easy to knead, that of the flow nature in a mold is good, and shows high intensity and high conductivity. Gas transmittance is also excellent in sealing nature low (only the value about an error has been measured). On the other hand, although the sample which uses polyamide as a resinous principle is easy to knead and the flow nature in a mold is also good, intensity is somewhat inferior and, moreover, volume resistivity has a

high fault (comparative examples 1-3). In the sample which uses polybutylene terephthalate and thermoplastic elastomer polyester as a resinous principle, it is inferior to the sample according to this invention also about kneading nature, flow nature, intensity, and conductive any (comparative examples 4 and 5). Although the volume resistivity of the raw material LCP resin itself used in the example is higher than the resin (polyamide, PBT, TPEE) used by the comparative example three sorts, the conductive resin composition obtained in spite of it has good conductivity.

[0025][Comparative example 6] Although the same operation as Examples 1-6 was tried except having used polycarbonate (volume resistivity 4x10 16 omega-cm, specific gravity 1.20, heat deflection temperature of 135 **) as a resinous principle, When 200 weight-section (about 67% of the whole) grade addition of the expanded graphite was carried out, it became powder state, and kneaded material overflowed from the kneading machine and it became impossible to kneading continue it.

[0026][Comparative example 7] Although the same operation as Examples 1-6 was tried except having used polystyrene (specific gravity 1.06, heat deflection temperature of 81 **) as a resinous principle, before adding about 200 weight sections of expanded graphite, it became powder state, and kneaded material overflowed from the kneading machine and it became impossible to kneading continue it.

[0027][Examples 7-17] As shown in Table 2, the constituent with LCP was prepared using various conductive fillers. Here, the mean fiber length of 1 d and glass fiber of the particle diameter of spherical silver powder is 0.2 mm, thickness is 3 mm, and the mean fiber length [of 0.1-1.0 micrometer and carbon fiber] of thickness is 2d. And the sheet-shaped sample was fabricated like Examples 1-6. The difficulty nature at the time of manufacturing each sample and the physical properties of a sample are shown in Table 2.

[0028]

表 2：各サンプルの製造容易性・物性

		実施例7	実施例8	実施例9	実施例10	実施例11	実施例12	実施例13	実施例14	実施例15	実施例16	実施例17
配合	LCP-1	25.0	25.0	25.0	25.0	25.0	25.0	20.0	20.0	20.0	20.0	20.0
	膨張黒鉛	50.0	50.0	50.0	50.0	50.0	50.0	80.0	70.0	50.0	50.0	50.0
	粒状黒鉛	25.0	—	—	—	—	—	—	10.0	30.0	25.0	25.0
	アセチレンブラック	—	25.0	—	—	—	—	—	—	—	—	—
	ケッチェンブラック	—	—	25.0	—	—	—	—	—	—	—	—
	SRFカーボン	—	—	—	25.0	—	—	—	—	—	—	—
	MTカーボン	—	—	—	—	25.0	—	—	—	—	—	—
	球状銀粉	—	—	—	—	—	25.0	—	—	—	—	—
	ピッチ系炭素繊維	—	—	—	—	—	—	—	—	—	5.0	—
	ガラス繊維	—	—	—	—	—	—	—	—	—	—	5.0
製造	混練難易	容易	容易	容易	容易	容易	容易	容易	容易	容易	容易	容易
	プレス内流れ性	良好	やや悪	やや悪	やや悪	やや悪	良好	良好	良好	良好	やや悪	良好
物性	曲げ強さ(kgf/cm²)	252	273	287	347	307	221	176	205	214	272	302
	体積固有抵抗(mΩ cm)	13	15	11	17	20	6	8	7	4	5	8

[0029]even if the conductive resin composition which uses LCP as a resinous principle according to this invention boils and changes various kinds of conductive filler, and loadings, it is easy to fabricate and it is clear that its high intensity and conductivity are shown.

[0030]

[Effect of the Invention]By this invention, manufacture and shaping were easy and the resin composition which is excellent in intensity, conductivity, and sealing nature, the cell for fuel which comprises it, and the sealing material were provided. In view of the

material which has these advantages not having been seen conventionally, the effect of this invention is remarkable.

[Translation done.]